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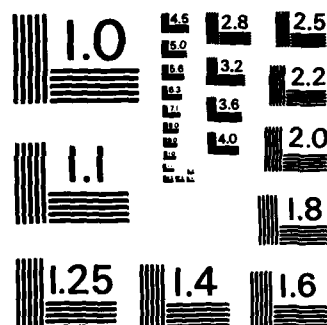
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Preparation of P-N-H and P-P Compounds
from a Silylated Amino(Methylene)phosphine

by

Bei-Li Li and Robert H. Neilson

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Texas Christian University
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Preparation of P-N-H and P-P Compounds from
a Silylated Amino(methylene)phosphine

Bei-Li Li and Robert H. Neilson*

Abstract

Secondary amines react with the silylated amino(methylene)-
phosphine $(\text{Me}_3\text{Si})_2\text{NP}=\text{CHSiMe}_3$ (1) by a complex process involving
Si-N bond cleavage as well as addition to the $\text{P}=\text{C}$ bond. Thus,
treatment of 1 with Et_2NH yields either the N-H phosphine
 $\text{Me}_3\text{SiN}(\text{H})\text{P}(\text{NET}_2)\text{CH}_2\text{SiMe}_3$ (2) or the unexpected PV-PIII product
 $\text{Me}_3\text{SiN}=\text{P}(\text{NET}_2)(\text{CH}_2\text{SiMe}_3)-\text{P}(\text{CH}_2\text{SiMe}_3)\text{N}(\text{SiMe}_3)_2$ (3), depending upon
the reaction stoichiometry. In two separate experiments with
mechanistic implications: (a) 2 was prepared from the reaction
of Et_2NH with $(\text{Me}_3\text{Si})_2\text{NP}(\text{NET}_2)\text{CH}_2\text{SiMe}_3$ (1a), the presumed
intermediate in the $\text{Et}_2\text{NH}/1$ reaction, and (2) 3 was prepared
directly by addition of the N-H compound 2 to the
(methylene)phosphine 1. Compound 2 is smoothly oxidized by CCl_4
to the P-chlorophosphoranimine $\text{Me}_3\text{SiN}=\text{P}(\text{Cl})(\text{NET}_2)\text{CH}_2\text{SiMe}_3$ (4) or
deprotonated by $n\text{-BuLi}$. The ambident anion thus formed reacts
with the chlorophosphines Ph_2PCl and $(\text{Me}_3\text{Si})_2\text{NP}(\text{Cl})\text{CH}_2\text{SiMe}_3$ to
yield the P-P products $\text{Me}_3\text{SiN}=\text{P}(\text{NET}_2)(\text{CH}_2\text{SiMe}_3)-\text{PPh}_2$ (5) and
compound 3, respectively.



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Introduction

The chemistry of 2-coordinate, acyclic p^{III} compounds containing the $P=C$ double bond, the (methylene)phosphines, is of considerable current interest.¹ Four major types of reactions of such compounds have been studied: (1) addition and cycloaddition reactions of the $P=C$ bond, (2) complexation of transition metals to the phosphorus lone pair and/or the $P-C$ π bond, (3) oxidation to the 3-coordinate p^V state, and (4) nucleophilic substitution at the 2-coordinate p^{III} center. Our recent studies,^{2,3} in particular, have shown that (methylene)phosphines bearing the disilylamino group, e.g., $(Me_3Si)_2NP=CHSiMe_3$ (**1**)⁴, actually exhibit all of these reaction pathways.

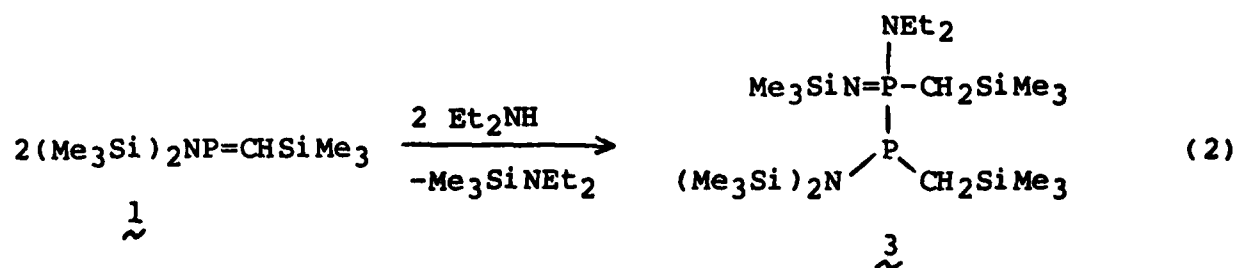
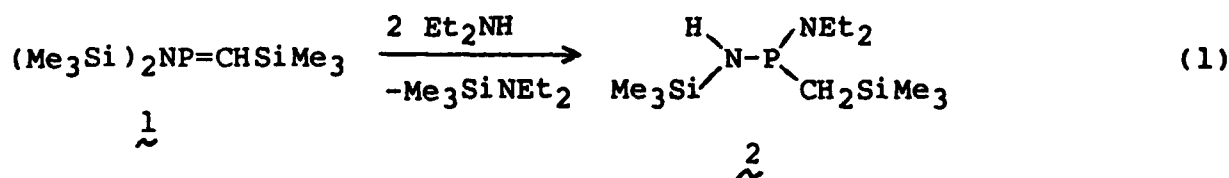
In addition, the Si-N bonds in compounds such as **1** are potentially reactive sites. The general lack of Si-N reactions in these 2-coordinate phosphines is rather surprising since many examples of silyl group rearrangement and/or elimination processes have been observed in 3- and 4-coordinate Si-N-P systems.⁵ We report here, however, the observation of Si-N bond cleavage as part of a complex series of reactions between **1** and diethylamine. Some related preparative chemistry is also described.

Results and Discussion

The reactions of the 2-coordinate phosphines $(Me_3Si)_2NP=E-SiMe_3$ ($E = CH, N$) with protic reagents generally occur either by simple (1,2)-addition to the double bond⁴ or by oxidative addition to the highly electrophilic phosphorus center.⁶ Therefore, we expected to find one or both of these pathways

operating in the reaction of 1 (E = CH) with secondary amines R₂NH (R = Et, n-Bu, i-Pr). A preliminary study of such reactions, however, in NMR-tube experiments, revealed an unexpected degree of complexity. The formation of the Si-N cleavage product Me₃SiNR₂ and mixtures of phosphorus-containing compounds was consistently observed. As a representative example, the reaction of 1 with Et₂NH was selected for more detailed study on a preparative scale.

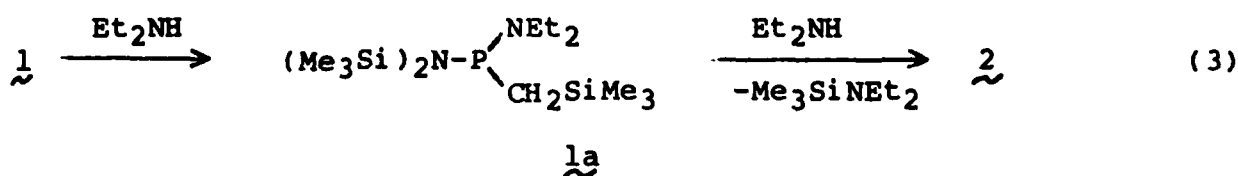
In a typical experiment, Et₂NH was added to a CH₂Cl₂ solution of 1 at 0°C with subsequent warming to room temperature. The ³¹P NMR spectra of the reaction mixture showed that two major products (2 and 3) were formed in a ratio that depended upon the reaction stoichiometry (eqs 1 and 2). Thus, from the



reaction of 1 with 2 equivalents of Et₂NH (eq 1), the N-H phosphine 2 was obtained in 59% yield by fractional distillation while the equimolar reaction (eq 2) afforded the unusual p^{III}-p^V product 3 in an isolated yield of 65%. In both cases, the

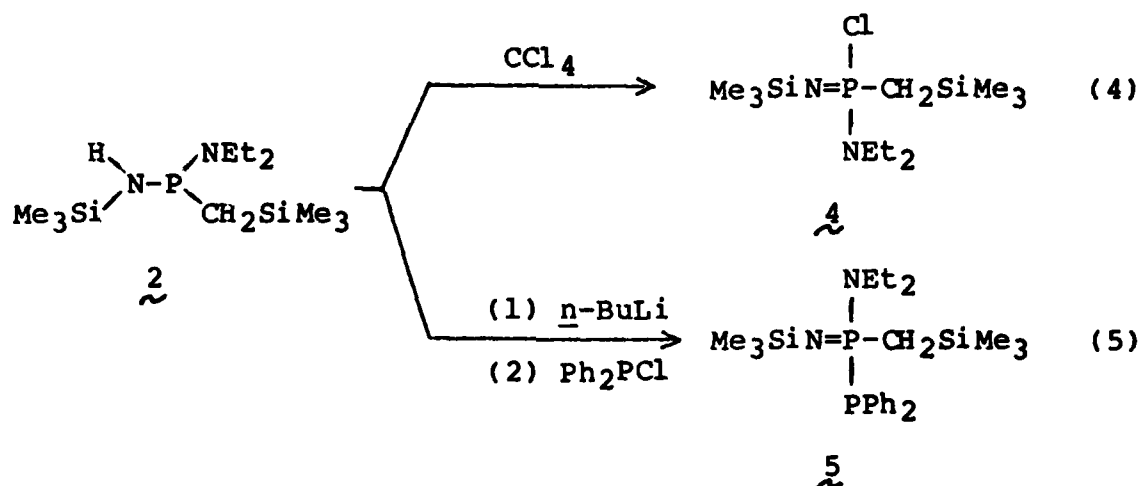
byproduct $\text{Me}_3\text{SiNEt}_2$ was identified in the solvent fraction by NMR spectroscopy.

The structure of compound 2 was readily assigned on the basis of NMR (Table I), IR, and mass spectral data. Moreover, some reactions involving 2 provide chemical evidence for its structure as well as its mode of formation from 1. Most likely, the production of 2 occurs via the intermediate formation of the (1,2)-addition product 1a (eq 3). Although 1a was not detected



by ^{31}P NMR among the reaction products, it is a stable compound (^{31}P δ 92) that has been prepared by an independent route.⁷ Treatment of an authentic sample of 1a with one equivalent of Et_2NH in CH_2Cl_2 solution rapidly and cleanly gives the Si-N cleavage product 2 (81% isolated yield).

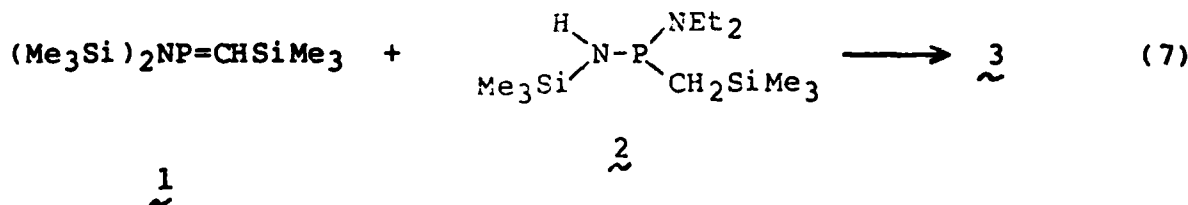
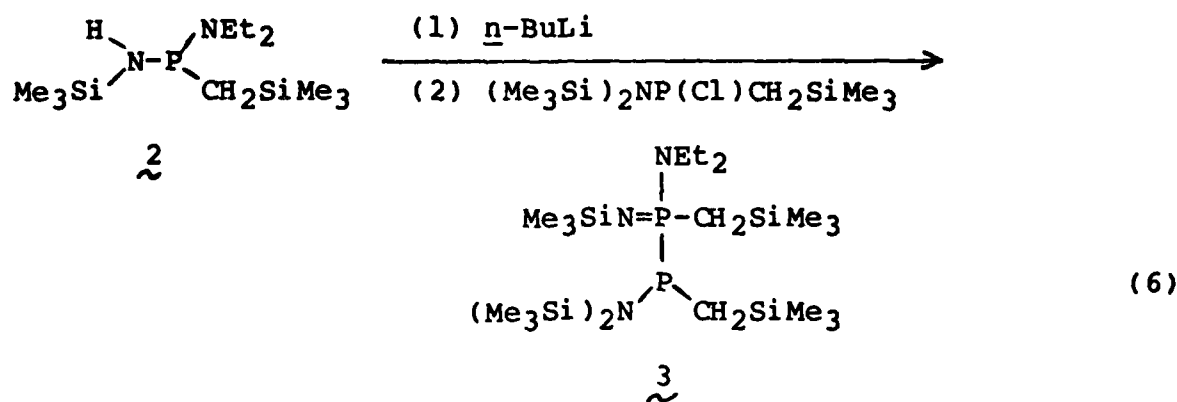
The $\text{P}^{\text{III}}\text{-N-H}$ functional group in 2 was confirmed by the characteristic reaction with CCl_4 ⁸ which afforded the P-chlorophosphoranimine 4 (eq 4) in 83% yield. In addition, the



ambident anion, generated by deprotonation of **2** with $n\text{-BuLi}$, reacted with Ph_2PCl (eq 5) to give the P-P bonded derivative **5**. The structure of **5**, a high-boiling liquid obtained in 61% yield, was confirmed by NMR spectral data. In particular, the ^{31}P NMR spectrum consists of an AB quartet with the J_{pp} value (209 Hz) and Ph_2P chemical shift (δ -19.3) being very similar to those of some close model compounds with the $\text{Ph}_2\text{P}-\text{P}^{\text{V}}$ linkage.^{9,10} The ^{13}C chemical shifts and J_{PC} values observed for the CH_2 and NEt_2 signals of **5** are also much more like those of the P^{V} analog **4** than the P^{III} compound **2**. These NMR data, therefore, preclude the possibility of **5** having the isomeric $\text{P}^{\text{III}}-\text{N}-\text{P}^{\text{III}}$ structure $\text{Ph}_2\text{PN}(\text{SiMe}_3)\text{P}(\text{NEt}_2)\text{CH}_2\text{SiMe}_3$. In fact, the Ph_2P group in that type of compound would be expected to have a ^{31}P chemical shift at much lower field (ca. 30-70 ppm).^{10,11}

Compound **5**, in turn, is a good structural and synthetic model for the P-P bonded product **3** obtained from the equimolar reaction of **1** with Et_2NH (eq 2). The large value of J_{pp} (290 Hz) found for **3** is especially indicative of the P-P bond. Also, it

was possible to synthesize 3 from the N-H phosphine 2 (eq 6) by the same method used for the preparation of the Ph₂P derivative 5. Moreover, compound 3 was produced quantitatively when the starting P=C reagent 1 was treated with the N-H derivative 2 (eq 7).



The latter finding accounts for how the P-P product 3 is formed in the reaction of 1 with an equimolar quantity of Et₂NH. It appears that 1 reacts first with 2 equivalents of Et₂NH to produce the Si-N cleavage product 2, probably via the (1,2)-addition product 1a. The unused 1 then reacts with 2, as shown in eq 7, to afford the final product 3.

Finally, it is interesting to note that compound 3 is the third different type of diphosphorus product to be derived from the (methylene)phosphine 1. We have previously reported that the reactions of 1 with Ph_2PCl or $\text{MeLi}/\text{Me}_3\text{SiCl}$ yield the diphosphinomethanes $(\text{Me}_3\text{Si})_2\text{NP}(\text{Cl})\text{CH}(\text{PPh}_2)\text{SiMe}_3^3$ and $\text{Me}_2\text{PCH}(\text{SiMe}_3)\text{P}(\text{Me})\text{CH}(\text{SiMe}_3)_2^2$, respectively. It seems clear, therefore, that amino(methylene)phosphines such as 1 are useful reagents for the preparation of more complex types of organophosphorus compounds. This preparative chemistry is under continuing study in our laboratory.

Experimental Section

Materials and General Procedures. Chlorodiphenylphosphine, *n*-BuLi (hexane solution), and CCl₄ were obtained from commercial sources and used as received. Diethylamine was dried over KOH and distilled prior to use. Ether, hexane, and CH₂Cl₂ were distilled from CaH₂ and stored over molecular sieves. The starting materials (Me₃Si)₂NP(X)CH₂SiMe₃ (X = Cl⁴, NEt₂⁷) were prepared and purified according to published procedures. Proton NMR spectra were recorded on a Varian EM-390 spectrometer; ¹³C and ³¹P, both with ¹H decoupling, were obtained in the FT mode on a JEOL FX-60 instrument. Infrared spectra were recorded on a Beckman 4250 spectrophotometer using neat liquid samples. Mass spectra were obtained on a Finnigan OWA 1020 GC-MS system. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

All reactions and other manipulations were carried out under an atmosphere of dry nitrogen or under vacuum. The procedures described herein are typical of those used for the preparation of the new compounds in this study.

(Diethylamino)(trimethylsilylamino)(trimethylsilylmethyl)-phosphine (2). (a) From (methylene)phosphine 1. Diethylamine (6.5 mL, 55 mmol) was added via syringe to a stirred solution of 1 (6.93 g, 25 mL) in CH₂Cl₂ (60 mL) at 0°C. The mixture was allowed to warm to room temperature and then stirred overnight. Solvent removal under vacuum left a cloudy liquid residue. The byproduct Me₃SiNEt₂ was identified in the solvent fraction by comparing its ¹H NMR spectrum to that of an authentic sample.

From the residue, 2 was obtained by fractional distillation through a 10-cm Vigreux column as a colorless liquid (4.1 g, 59% yield, bp 72-75°C/0.9 mm). The NMR data are summarized in Table I. On standing at room temperature for a few days, compound 2 deposited some unidentified white solids, presumably P-N-P condensation products, and evolved Me₃SiNEt₂. Due to this thermal instability it was not submitted for elemental analysis. Its derivatives 4 and 5, however, did give satisfactory analyses (see below). The IR spectrum of 2 contained the characteristic N-H stretching band at 3320 cm⁻¹. Mass spectrum, m/e (relative intensity): 278(7.8) (M⁺), 263(8.2), 192(76.2), 146(45.7), 130(35.4), 118(45.7), 74(93.6), 59(41.2), 45(100). (b) From (Me₃Si)₂NP(NEt₂)CH₂SiMe₃ (1a). In a similar manner, compound 1a (7.0 g, 20 mmol) in CH₂Cl₂ (50 mL) was treated with Et₂NH (4.5 mL, 40 mmol) at 0°C. After stirring overnight at room temperature, work up as described above gave 2 as a colorless liquid (4.5 g, 81% yield, bp 71-74°C/1.0 mm) having the same NMR spectral data as the sample prepared above.

P-Diethylamino-P-(trimethylsilylmethyl)-P-{[Bis(trimethylsilyl)amino](trimethylsilylmethyl)phosphino}-N-(trimethylsilyl)-phosphoranimine (3). (a) From 1 and Et₂NH. Diethylamine (3.1 mL, 30 mmol) was added via syringe to a stirred solution of 1 (8.3 g, 30 mmol) in CH₂Cl₂ (30 mL) at 0°C. After warming to room temperature and stirring overnight, solvent removal left a white solid/liquid residue. Fractional distillation gave a major fraction with bp 70-75°C/0.01 mm that solidified in the receiving flask and the condenser. The solids were combined by washing the

condenser and flask with CH_2Cl_2 . Solvent removal left 3 as a wax-like solid (5.4 g, 65% yield). Anal. Calcd: C, 45.36; H, 10.70. Found: C, 45.56; H, 10.77. (b) From 1 and 2. Equimolar quantities (3.5 mmol) of compounds 1 and 2 were combined at 0°C in CH_2Cl_2 (6 mL). After stirring 4 h at 0°C , ^{31}P NMR indicated that no reaction had occurred. The mixture was then allowed to warm to room temperature and was stirred overnight. At this point, the quantitative formation of product 3 was confirmed by the AB quartet pattern in the ^{31}P NMR spectrum (Table I). (c) From 2 and $n\text{-BuLi}$, etc. $n\text{-Butyllithium}$ (3.2 mL, 2.6 M, 8.3 mmol) was added via syringe to a stirred solution of 2 (2.2 g, 7.9 mmol) in Et_2O (12 mL) at -78°C . The mixture was allowed to warm to room temperature and was stirred for ca. 10 min. After cooling the mixture to 0°C , $(\text{Me}_3\text{Si})_2\text{NP}(\text{Cl})\text{CH}_2\text{SiMe}_3$ (2.8 mL, 8 mmol) was added via syringe. A white precipitate formed immediately. The mixture was then stirred overnight at room temperature, filtered under nitrogen, and freed of solvent. Hexane (ca. 20 mL) was added in order to extract the product from additional solids that had formed. Following another filtration and solvent removal, distillation through a short path apparatus gave 3 as a colorless liquid (2.2 g, 50% yield), bp $90\text{--}92^\circ\text{C}/0.05$ mm, that solidified on standing.

P-Chloro-P-diethylamino-P-(trimethylsilylmethyl)-N-(trimethylsilyl)phosphoranimine (4). Carbon tetrachloride (2 mL, ca. 20 mmol) was added to a stirred solution of 2 (2.8 g, 10.0 mmol) in CH_2Cl_2 (10 mL) at 0°C . After warming to room temperature and stirring overnight, fractional distillation gave

4 as a colorless liquid (2.6 g, 83% yield, bp 66-67°C/0.05 mm).

Anal. Calcd: C, 42.28, H, 9.69. Found: C, 42.50; H, 9.93.

P-Diethylamino-P-(trimethylsilylmethyl)-P-diphenylphosphino-
N-(trimethylsilyl)phosphoranimine (5). The same procedure (12
mmol scale) as that described above for the preparation of 3
(method c) gave 5 as a colorless, viscous liquid (3.4 g, 61%
yield, bp 142-148°C/0.05 mm). Anal. Calcd: C, 59.70; H, 8.72.
Found: C, 59.30; H, 8.90.

Acknowledgment. We thank the U.S. Office of Naval Research
and the Robert A. Welch Foundation for generous financial
support.

References and Notes

- (1) For example, see the following and references cited therein:
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- (4) Neilson, R.H. Inorg. Chem. 1981, 20, 1679.
- (5) See, for example:
 - (a) Ford, R.R.; Goodman, M.A.; Neilson, R.H.; Roy, A.K.; Wettermark, U.G.; Wisian-Neilson, P. Inorg. Chem. 1984, 23, 2063.
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- (7) Thoma, R.J. Ph.D. Dissertation, Texas Christian University, Fort Worth, TX, 1984. Several other Si-N cleavage reactions, similar to the conversion of 1a to 2, have been observed in our laboratory.

(8) For other examples see:

(a) O'Neal, H.R.; Neilson, R.H. Inorg. Chem. 1984, 23, 1372.

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(11) For example, the ^{31}P shift of $\text{Ph}_2\text{PN}(\text{SiMe}_3)_2$ is δ 49. Noth,
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Table I. NMR Spectroscopic Data^a

compound	signal	¹ H		¹³ C		³¹ P
		δ	J _{PH} ^b	δ	J _{PC}	δ (J _{PP})
$ \begin{array}{c} \text{Me}_3\text{Si} \quad \text{NEt}_2 \\ \diagdown \quad \diagup \\ \text{N}-\text{P} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{CH}_2\text{SiMe}_3 \end{array} $ <p>2</p>	Me ₃ SiC	0.06	0.8	-0.06	5.5	68.5
	Me ₃ SiN	0.11	0.8	1.32	5.5	
	PCH ₂	0.88	1.8	24.69	25.6	
	NCH ₂ CH ₃	1.03	(7.1)	15.41	5.5	
	NCH ₂ CH ₃	2.90	8.6	41.16	16.5	
$ \begin{array}{c} \text{NEt}_2 \\ \\ \text{Me}_3\text{SiN}=\text{P}^1-\text{CH}_2\text{SiMe}_3 \\ \\ \text{P}^2 \\ / \quad \backslash \\ (\text{Me}_3\text{Si})_2\text{N} \quad \text{CH}_2\text{SiMe}_3 \end{array} $ <p>3</p>	(Me ₃ Si) ₂ N	0.07		4.63		P ¹ , 26.9
		0.18		5.85		P ² , 38.0
	Me ₃ SiN	0.15	2.4	3.86	3.6	(290)
	Me ₃ SiC	-0.03		0.00		
		0.03		0.53		
	PCH ₂	0.9-1.3 ^c		13-25 ^c		
	NCH ₂ CH ₃	0.93	(7.2)	14.80	1.8	
	NCH ₂ CH ₃	2.7-3.1 ^c		38.68	4.9, 6.0	
$ \begin{array}{c} \text{NEt}_2 \\ \\ \text{Me}_3\text{SiN}=\text{P}-\text{CH}_2\text{SiMe}_3 \\ \\ \text{Cl} \end{array} $ <p>4</p>	Me ₃ SiC	0.09		-0.10	4.3	17.2
	Me ₃ SiN	0.20		2.84	4.5	
	PCH ₂	1.66	22.2	27.15	116.6	
		1.58	20.4			
	NCH ₂ CH ₃	1.12	(7.2)	13.18	5.5	
	NCH ₂ CH ₃	2.8-3.4 ^c		38.97	3.1	

Table I. continued.

$ \begin{array}{c} \text{NEt}_2 \\ \\ \text{Me}_3\text{SiN}=\text{P}^1-\text{CH}_2\text{SiMe}_3 \\ \\ \text{Ph}_2\text{P}^2 \\ \sim 5 \end{array} $	Me ₃ SiC	-0.17	0.6	-0.19	3.9	P ¹ , 17.1
	Me ₃ SiN	0.06	0.6	2.76	4.9	P ² , -19.3
	PCH ₂	0.09- 1.3 ^c		27.13	116.2	(209)
	NCH ₂ CH ₃	0.93	(7.2)	13.12	5.9	
	NCH ₂ CH ₃	2.7- 3.2 ^c		38.95	2.9	
	Ph	7.2- 7.9 ^c		127- 134 ^c		

^aChemical shifts downfield from Me₄Si for ¹H and ¹³C spectra and from H₃PO₄ for ³¹P spectra; coupling constants in Hz. Solvents: ¹H and ³¹P, CH₂Cl₂; ¹³C, CDCl₃.

^bValues in parentheses are J_{HH}.

^cComplex multiplet.

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